



Experimental study of nanoparticles as catalyst in enhancing matrix acidizing for carbonate reservoir

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Abstract

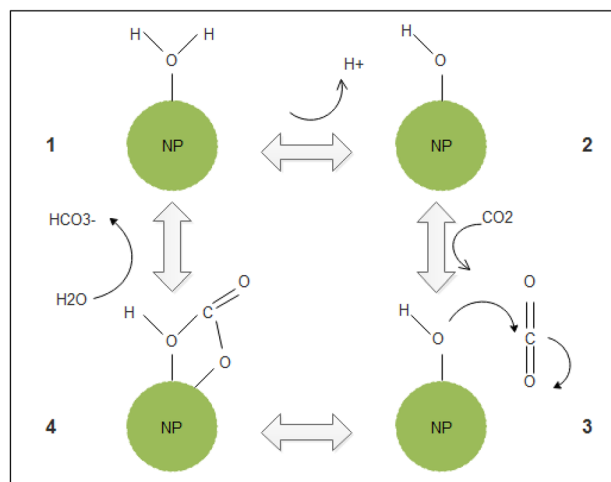
Hydrochloric (HCl) acid is the most common stimulating fluid used in acidizing job due to its strong acidic property and low cost to create or enlarge existing wormhole within the reservoir. However, the HCl acid has rapid reaction with carbonate reservoir, and it is causing surface dissolution of the rock and lowering the penetration into the formation. Recent studies have shown the addition of nickel nanoparticles as catalyst to handle the problems in HCl acidizing. The nanoparticles are high-performance catalyst due to their high ratio of surface area to volume. The proposed method in this research is to mix the nanoparticles with the carbonate formation prior to the acid injection into the formation. The efficiency of the nanoparticles as catalyst depends on the thermodynamics property, which is surface energy of the materials used. The surface energy reduces as the size of particles become smaller. However, the effect of surface energy become insignificant on nanoparticles due to the small particles sizes, and the surface energy is based on the individual energy of the particles. Therefore, this research investigates the efficiency of silica, aluminum oxide, and zinc oxide besides nickel nanoparticles based on their thermodynamics property in accelerating the conversion of CO₂ gas into carbonic acid. The approach consists of investigating the efficiency of nanoparticles in different concentrations of carbonate and mass of nanoparticles. Suitable nanoparticles are proposed based on efficiency and cost in retarding the HCl reactivity and rapid formation of in situ carbonic acid. The concentration of carbonic acid (H₂CO₃), bicarbonate ion (HCO₃⁻), and carbonate ion (CO₃²⁻) is analyzed based on Henry's law of solubility. The result shows that the silica has the best efficiency as catalyst in 6700 ppm Na₂CO₃ solution due to its high stability and dispersion in aqueous solution. The silica engages into rapid dissociation of water molecules and bind with OH⁻ group to react with CO₂ gas and form HCO₃⁻. The nanoparticles reduce the reactivity of HCl through conversion of bicarbonate ions. However, ZnO gives better efficiency in 17,000 ppm of Na₂CO₃. The efficiency of silica in this concentration increased at 0.7 g, proving the minimum amount required as catalyst. In contrast, ZnO and Al₂O₃ have lower efficiency as acid retarder since changes in pH values affect the performance of the nanoparticles. The surface charge demonstrated by ZnO and Al₂O₃ depends on pH changes which makes these nanoparticles to perform inefficiently. The silica is chosen as the best catalyst due to high efficiency versus cost ratio.

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Graphical Abstract

Conversion of CO₂ Gas into Carbonic Acid by Nanoparticles

Keywords Henry's law of solubility · Matrix acidizing · Nanoparticles · Catalysts · CO₂ gas · Carbonic acid

Introduction

Carbonates reservoirs possess heterogeneous properties in both horizontal and vertical directions, with natural fractures, permeability barriers, and huge array of porosity types (Izgec et al. 2008). Matrix acidizing is executed to create or enlarge existing wormhole by using hydrochloric acid (HCl) due to high dissolution into carbonate rock and lower cost (Mahmoud et al. 2010; Chang et al. 2008; Bartko et al. 2007; Huang et al. 2000). However, HCl has high corrosive property that tends to corrode well tubular and rapid reaction at the surface of carbonate rock (Izgec et al. 2008; Chang et al. 2008). The release of CO₂ gas by-product between the reaction of HCl and carbonate rock has high adhesive force and forms barrier between acid and rock due to high adhesive force (Raj and Pal 2014). Expensive corrosion tubulars are unsuccessful in protecting the well at high temperature for longer time. The HCl acid also has high reaction with carbonate rock, which creates surface dissolution and low penetration (Raj and Pal 2014). Organic additives and modified acids are added to retard and reduce corrosiveness of HCl (Huang et al. 2000; Nasr-El-Din and Al-Mohammed 2006; Zakaria and Nasr-El-Din 2016; Amro 2006). These modified acids are used to corrosion inhibitor for wells besides improving the acid penetration into the formation. The drawback of organic acid is low dissolving capacity in the HCl, and longer time is taken to design suitable organic acid (Raj and Pal 2014). In conjunction with few researches on incorporating nanoparticles in alleviating these problems, this study proposes a detailed investigation on aluminum

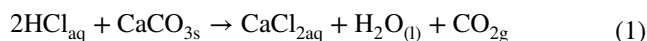
oxide (Al₂O₃), zinc oxide (ZnO), and silica (SiO₂) nanoparticles as catalysts to retard the HCl reaction and accelerate the in situ conversion of CO₂ gas into carbonic acid. The nanoparticles are high-performance catalyst due to their high ratio of surface area to volume. The objectives of this research are to (1) determine the efficiency of HCl reaction in carbonate with and without the presence of nanoparticles, (2) analyze and identify suitable nanoparticles in catalytic reaction to enhance the matrix acidizing, (3) interpret contributing properties of nanoparticles in the catalytic reaction, and (4) propose suitable nanoparticles based on cost and efficiency.

Background

Carbonate reservoirs and matrix acidizing

Carbonate reservoir faces continuous diagenesis due to high-pressure increase on burial and results into physical compacted and natural fractures (London 2017). The severity of fractures is further increased by drilling and completion processes (Morsy et al. 2015). These complexities of carbonate formation are (1) heterogeneous in vertical and horizontal reservoir property, (2) natural fractures and permeability barriers, and (3) porosity ranging from intercrystalline to massive vugular and cavernous porosity (Raj and Pal 2014). The severity of fractured pore networks in carbonate reservoir increases the barrier for fluid flow (Jones 1975; Popov et al. 2007; Philip et al. Philip et al. 2005). Matrix acidizing

is introduced by injecting acid stimulated fluid, i.e., HCl, into reservoir below fracture pressure to enhance reservoir conductivity and improve the flow rate through dissociation of the reservoir rock (Izgec et al. 2008; Chang et al. 2008; Raj and Pal 2014; Morsy et al. 2015; Company 2013; Gomez 2006; Kalia and Balakotaiah 2010; Al-Hadhrani and Blunt 2000; Rahim et al. 2014; Runtuwene et al. 2010). The HCl acid spreads efficiently in carbonate formation compared to homogeneous reservoir due to the flow properties, which varies from small (micron) to larger (centimeter) scale (Izgec et al. 2008). The wormhole operates to transport reservoir fluid within matrix into the wellbore by overcoming formation damage and low permeability (Rahim et al. 2014). This effectiveness is limited as HCl acid has strong acidic property, which corrodes the well tubular and reacts almost instantly with carbonate rock causing surface dissolution of formation (Chang et al. 2008). The instantaneous reaction fails to meet the main objective of matrix acidizing to create deeper penetration into the formation. CO_2 , which is a by-product of HCl reaction with carbonate formation as shown in Eq. (1), caused formation barrier due to high adhesive force (Raj and Pal 2014; Frenier and Hill 2002).



Carbonic acids are common alternatives to lower the reaction of HCl besides reducing the corrosiveness on well tubulars (Chang et al. 2008; Huang et al. 2000; Amro 2006; Buijse et al. Buijse et al. 2004; Yang et al. 2012). Despite the efficiency, carbonic acid buffers the pH of organic acid which causes incomplete dissociation of HCl. This defeats the sole reason of HCl usage since matrix acidizing cost increases as carbonic acid is much expensive compared to HCl for equivalent amount of rock dissolved (Chang et al. 2008; Raj and Pal 2014). Modified acid is investigated on improving the efficiency of matrix acidizing (Zakaria and Nasr-El-Din 2016; Al Otaibi et al. 2013; Carpenter 2014). The study does not comprehend the issue of CO_2 gas release from the reaction between HCl acid and carbonate rock.

Nanoparticles in catalytic reaction

To alleviate these problems, studies and researches have included nanoparticles in oil recovery process to improve the oil flow (El-Diasty and Aly 2015; Ogolo et al. 2012; Benetzen and Mogensen 2014; Idogun et al. 2016; Zhang et al. 2010; Negin et al. 2016). Nanoparticles are further developed as catalyst to solve the rapid reaction of HCl and CO_2 gas production in matrix acidizing for carbonate reservoir (Raj and Pal 2014). The proposed research has used nickel nanoparticles to accelerate the conversion of in situ organic acid from CO_2 gas, which reduces the need of expensive well tubulars and organic retarders (Ogolo et al. 2012; Bhaduri et al. 2015). Throughout the acidizing job, the nanoparticles

do not undergo any changes physically and remain the same after the reaction has occurred. Once CO_2 gas is released, NPs get into action as shown in Fig. 1.

As soon as the reaction between HCl acid and carbonate rock releases CO_2 gas, the nanoparticles convert the gaseous CO_2 into carbonic acid (aqueous CO_2) based on Eq. (2).



Referring to Eq. (3), the aqueous CO_2 will then bind with water molecules to produce strong carbonic acid.



The generated carbonic acid will undergo further dissociation into hydrogen and bicarbonate ion in case of weaker concentration as shown in Eq. (4).



In case of weaker ionic bonding, the nanoparticles will further break the bicarbonate ion into hydrogen and carbonate ions based on Eq. (5).



The catalytic reaction repeats as a cycle to ensure constant formation of carbonic acid while CO_2 gas is released. Catalyst is preferred to convert CO_2 gas into carbonic acid as lower activation energy is required. The efficiency of nanocomposite metal as catalyst depends on three criteria: (1) high surface area exposed to the reaction, (2) size and distribution of NPs should be uniform, and (3) nanoparticles presented in the substrate should be easily accessible to various chemical reagents (Patel et al. 2007). Nanoparticles

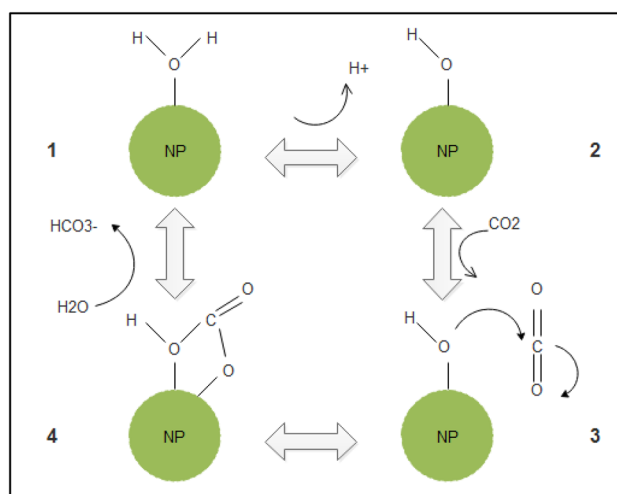


Fig. 1 Conversion of CO_2 gas into carbonic acid by nanoparticles (Raj and Pal 2014)

act as good catalyst due to ratio of surface area to volume. Diffusion and reaction rate at nanoscale, nanomaterials, and nanodevices occur more rapidly compared to larger size of material (Ogolo et al. 2012; Bennetzen and Mogensen 2014; Chaturvedi et al. 2012). The efficiency of nanoparticles is a function of on their hydrophobicity (contact angle), size, shape, and degree of agglomeration since these parameters influence the behavior of NPs at air/water interface (Blute et al. 2009). This research requires further improvement since nickel nanoparticles are chosen due to its wide usage in industries as catalyst. Nickel also has strong electromagnetic property, which creates adhesive force, which causes blockage in pore channels (Wu and Chen 2003).

Method

Experimental setup

Figure 2 shows the experimental setup by wrapping 2-L beaker with cotton wool and aluminum foil to prevent heat lost to the surrounding. An airtight cap is made and sealed with high-density polyethylene (HDPE) materials to avoid air leakage. Four (4) holes are then drilled to place pH meter, gas pressure sensor, K-type thermowires, and burette. Silicon sealants and grease are applied to enclose the gaps. Leak detector is then poured around the cap as shown in Fig. 3 to observe any formation of bubble as an indicator of leakage.

Calibrations are done on gas pressure sensor, pH meter, and K-type thermometer prior to the acidizing runs.

Materials

The diluted sodium carbonate (Na_2CO_3) at 6700 ppm is obtained by mixing 600 ml of distilled water with 4 g of Na_2CO_3 powder. Meanwhile, the concentration of diluted sodium carbonate at 17,000 ppm is obtained by mixing 600 ml with 7 g of Na_2CO_3 powder. Initial concentration of hydrochloric (HCl) acid is diluted to achieve concentration at 5% based on Eqs. 7 and 8.

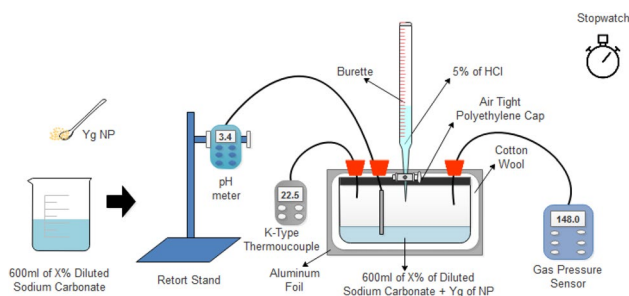


Fig. 2 Experimental setup

$$\text{No of moles (mol)} = \frac{\text{Mass (g)}}{\text{Molar Mass} \left(\frac{\text{g}}{\text{mol}} \right)} \quad (6)$$

$$C_p(\%) = C_m \times 100\% \times \frac{M}{\rho} \quad (7)$$

where C_p is concentration of HCl acid after dilution, C_m is molarity of HCl acid after dilution, mol, M is molecular weight of HCl, g/mol, and ρ is density of HCl acid, g/ml. Acidizing runs are conducted with and without the presence of nanoparticles. Manipulated variables used in this experiment are mentioned in Table 1.

The nanoparticles tabulated in Table 1 were chosen considering their proven performance as catalysts. Nickel oxide was studied by Raj and Pal (2014), and the outcome is quite promising.

Concentration of Carbonic Acid, Bicarbonate Ion and Carbonate Ion

Based on pH values measured in each run, the dissociation of hydrogen ions is calculated as shown in Eq. (8)

$$[\text{H}^+] = 10^{-\text{pH}} \quad (8)$$

The concentration of carbonic acid (H_2CO_3) is calculated based on the partial pressure of CO_2 gas, atm, and Henry's law of solubility of CO_2 in water, K_0 , L.atm/mol as shown in Eq. (9)

$$K_0 = \frac{[\text{H}_2\text{CO}_3]}{\text{PCO}_2} \quad (9)$$

Fig. 3 Airtight cap sealed with silicon sealant

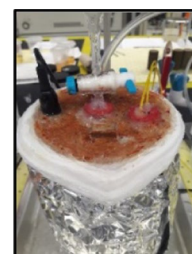


Table 1 Manipulated variable

Nanoparticles	Mass of nanoparticles (g)	Concentration of diluted sodium carbonate solution (ppm)
Al_2O_3	0.01	6700
SiO_2	0.1	17,000
ZnO	0.4	
	0.7	

In Eq. (10), the concentration of bicarbonate ion (HCO_3^-) is calculated based on concentration of hydrogen ion and carbonic acid with Henry's law of solubility of HCO_3^- ions, K_1 L.atm/mol

$$K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad (10)$$

Then, the concentration of carbonate ion (CO_3^{2-}) is determined by using Eq. (11)

$$K_2 = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (11)$$

The study is using diluted sodium carbonate rather than carbonate core. This simplifies the measurement and hence the calculation.

Results and discussion

Acidizing runs with nanoparticles in 6700 ppm Na_2CO_3

Based on Fig. 4, SiO_2 gives lower depletion in pH values for 0.01 g of nanoparticles in 6700 ppm concentration of diluted Na_2CO_3 solution. Meanwhile, the pH values dropped immediately after 100 s for Al_2O_3 NPs, while ZnO NPs gave pH depletion trend line similar to acidizing run without NPs.

In Fig. 5, SiO_2 nanoparticles show slowest depletion in pH, while ZnO nanoparticles show rapid dissociation of HCl compared to Al_2O_3 . Initially, ZnO nanoparticles give minimal reduction in pH till the values suddenly dropped below 3 at 2.5 min. Al_2O_3 nanoparticles show gradual decrease in pH before the reaction becomes slower.

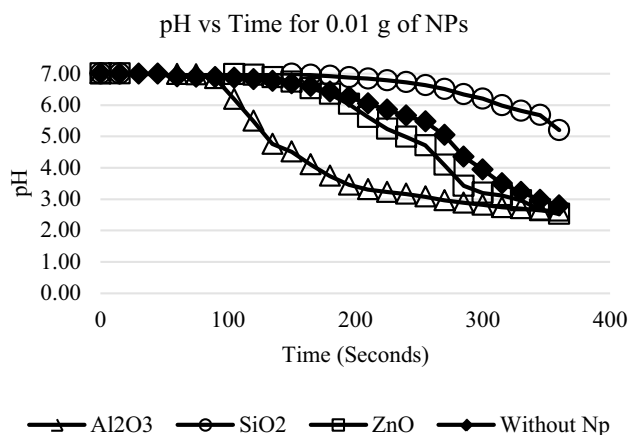


Fig. 4 pH versus time for 0.01 g NPs in 6700 ppm Na_2CO_3

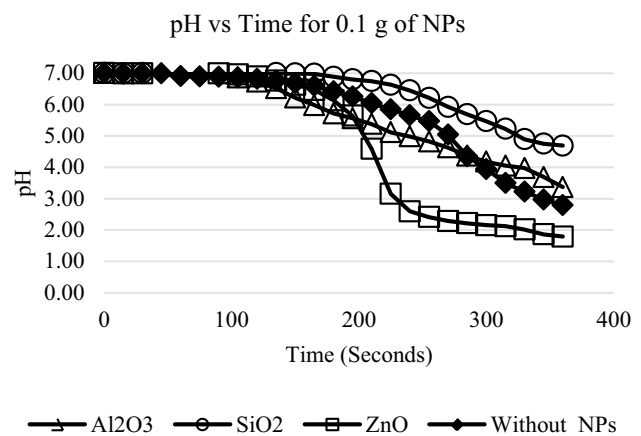


Fig. 5 pH versus time for 0.1 g NPs in 6700 ppm Na_2CO_3

Referring to Fig. 6, SiO_2 remained as the best catalyst to retard the reactivity of HCl as the amount of nanoparticles is increased to 0.4 g. ZnO gives almost similar reduction in pH as in SiO_2 , while rapid drop in pH values is observed for Al_2O_3 nanoparticles.

The SiO_2 gives minimal reduction in pH when 0.7 g of nanoparticles is added into 6700 ppm Na_2CO_3 as shown in Fig. 7. The pH values reduced slightly for Al_2O_3 initially for 2 min and generated inconsistent pattern afterward due to stability issue. ZnO nanoparticles give better reaction compared to Al_2O_3 in reducing the HCl reaction.

Overall for 6700 ppm concentration of diluted sodium carbonate solution, silica shows the best efficiency as acid retarder, followed by zinc oxide and aluminum oxide nanoparticles. Silica has shown consistent performance in reducing the HCl reaction with sodium carbonate as the amounts are increased.

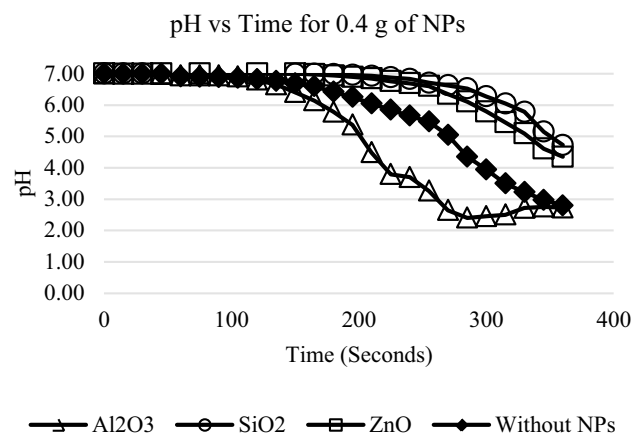


Fig. 6 pH versus time for 0.4 g NPs 6700 ppm Na_2CO_3

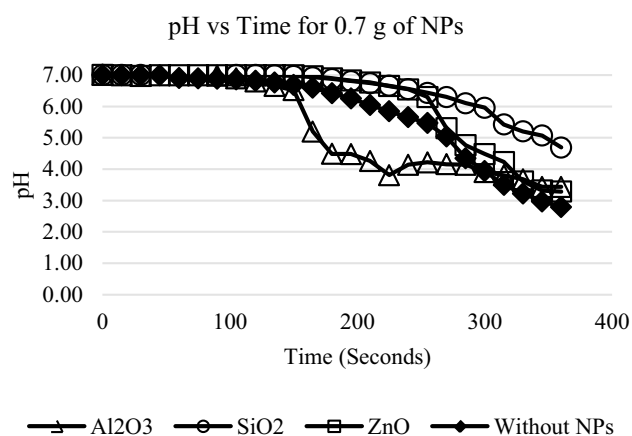


Fig. 7 pH versus time for 0.7 g NPs in 6700 ppm Na_2CO_3

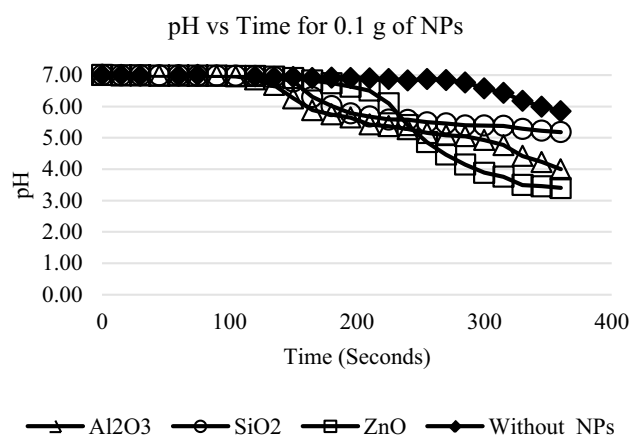


Fig. 9 pH versus time for 0.1 g NPs in 17,000 ppm Na_2CO_3

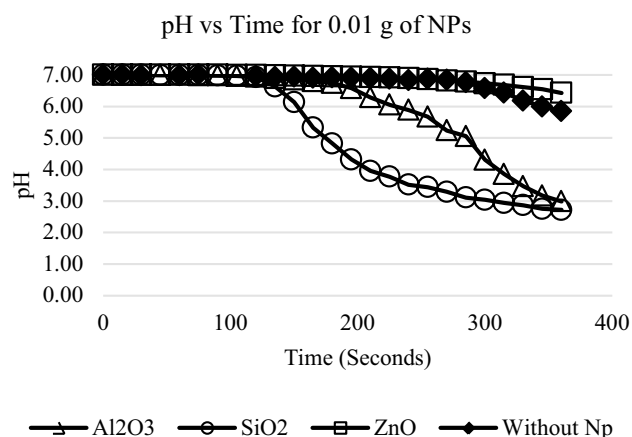


Fig. 8 pH versus time for 0.01 g NPs in 17,000 ppm Na_2CO_3

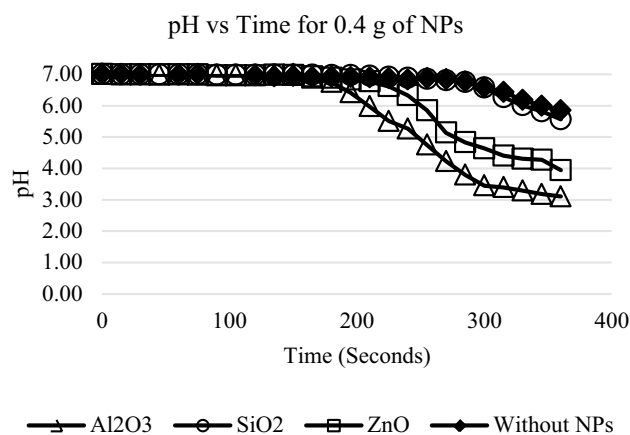


Fig. 10 pH versus time for 0.4 g NPs in 17,000 ppm Na_2CO_3

Acidizing runs with nanoparticles in 17,000 ppm Na_2CO_3

Based on Fig. 8, ZnO gives minimal reduction in pH of the solution for 0.01 g of nanoparticles added in 17,000 ppm Na_2CO_3 . In contrast with acidizing runs for 6700 ppm Na_2CO_3 , Al_2O_3 gives better performance as catalyst compared to silica nanoparticles. SiO_2 nanoparticles give constant depletion in pH before the values decrease gradually after 100 s. For lower amount of nanoparticles in 17,000 ppm, ZnO gives the best efficiency as catalyst.

All the three nanoparticles gave low performance as the amount is increased to 0.1 g based on Fig. 9. For the first 130 s, ZnO, SiO_2 , and Al_2O_3 nanoparticles show constant pH reading. Aluminum oxide reduced the pH values first, followed by SiO_2 and ZnO. ZnO gives constant pH of solution until the values dropped at 240 s. The depletion

of pH is constant after 150 s for SiO_2 , while Al_2O_3 shows better performance than ZnO after 200 s. Overall, Silica gave consistent performance compared to ZnO and Al_2O_3 although the nanoparticles did not retard the reactivity of HCl with diluted sodium carbonate solution.

Silica shows slight reduction in pH compared to acidizing runs without nanoparticles in Fig. 10. ZnO gives rapid depletion in pH values compared to silica. The lowest efficiency of catalytic reaction is demonstrated by Al_2O_3 . By increasing the amount of silica in 17,000 ppm Na_2CO_3 , the efficiency of the nanoparticles as catalyst can be increased.

The pH values remained almost constant with the presence of 0.7 g silica in 17,000 ppm Na_2CO_3 solution as shown in Fig. 11. Al_2O_3 demonstrated consistent pH trend for the first 180 s before the values dropped rapidly. Initially, ZnO gave rapid drop in pH values before the reduction becomes minimal after 200 s.

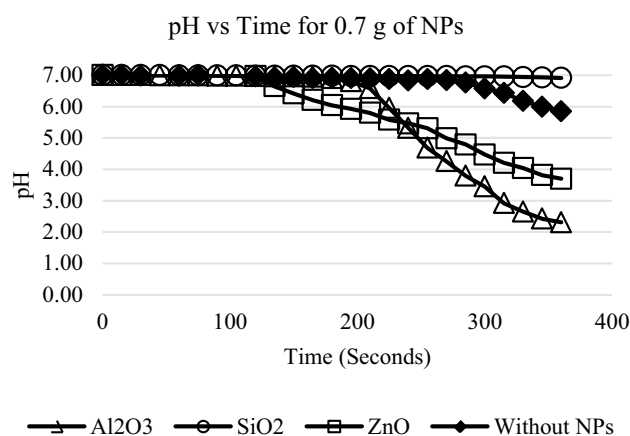


Fig. 11 pH versus time for 0.7 g NPs in 17,000 ppm Na_2CO_3

Performance of nanoparticles in 6700 ppm and 17,000 ppm Na_2CO_3

The efficiency of metal oxide nanoparticles as catalyst depends on the surface charge demonstrated as pH of solution changes. Based on thermodynamics law, the surface energy decreases as size of particles decreases. However, the effect of surface charge becomes insignificant as size of particles reduces in nanoscale. The surface charge demonstrated by nanoparticles is larger compared to bulk material due to size-dependent lattice parameter (Nanda et al. 2003). The reduction in particle size causes the surface energy demonstrated by individual particles in nanoscale become significant and yields larger energy.

Initially, Al_2O_3 nanoparticles show negative charge since the pH is high and attracted more H^+ from HCl, which resulted in low reaction with Na_2CO_3 . As the solution reached neutral pH, the surface charge for these nanoparticles becomes zero and caused HCl to dissociate H^+ rapidly (Gulicovski et al. 2008). This solution turns acidic immediately due to abundance of hydrogen ions reacting with Na_2CO_3 . The reaction is further accelerated by Al_2O_3 as the surface charge becomes positive in low pH. At this point, the nanoparticles attract hydroxyl (OH^-) ion from water molecules to form HCO_3^- through bonding with CO_2 gas.

Meanwhile, ZnO nanoparticles in water show a different property as the surface of the oxide is hydrolyzed and forms buildup of hydroxide layer (Reed 1986; Xu and Wang 2011). The changes in pH are minimal since the dissociation of ZnO into Zn^{2+} is most stable due to ionic equilibrium between zinc ion and zinc hydroxide. As ZnO binds with hydroxyl group from water in the beginning, the pH values drop gradually. Between pH at 4 and 6 for each case, ZnO gives unstable electrostatic charge due to buildup of unstable colloidal particles of $\text{Zn}(\text{OH})_2$ as a result of ionization (Degen and Kosec 2000). The depletion of pH becomes

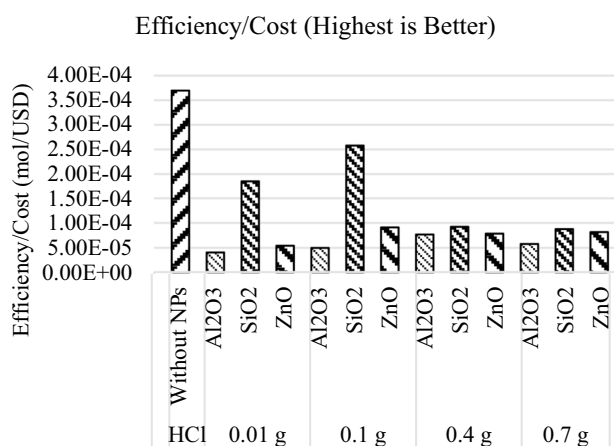


Fig. 12 Efficiency versus cost ratio of NPs in 6700 ppm Na_2CO_3

constant at the end of each run since ZnO nanoparticles have achieved stable surface charge. It is observed that:

- Nanoparticles acts as good corrosion inhibitor
- Nanoparticles are capable to be good retarder for acidic mud
- Nanoparticles are affected by thermal condition

Overall, SiO_2 shows the best performance as catalyst due to its stability in dispersing within the sodium carbonate solution (Kissa 1999; Asay and Kim 2005; Yalamanchili et al. 1996; Metin et al. 2011; Zhuravlev 1987). Once the nanoparticles are mixed with diluted sodium carbonate solution, silica immediately engages with dissociation of hydrogen and hydroxyl ions from water molecules to form silanol group (Si-OH) (Hofmann and Wilm 1934). The silanol group has strong hydrophilic properties that binds into hydrogen (H^+) ions which were dissociated from HCl to prevent the ions from fully spent. The reaction is further improved due to larger surface area of hydrophilic tail exposed to the reaction between HCl and sodium carbonate.

Efficiency versus cost ratio of nanoparticles in 6700 ppm and 17,000 ppm Na_2CO_3

For the acidizing run without the addition of nanoparticles, the total bicarbonate ion remained in the solution is divided with cost of HCl to yield efficiency versus cost ratio (mol/USD). The efficiency of nanoparticles in both cases is evaluated based on the remaining concentration bicarbonate ion in the solution and cost of each nanoparticle.

Based on Fig. 12, silica gives highest efficiency versus cost ratio. Silica shows higher concentration of HCO_3^- ion remaining in the solution due to rapid ionization between water and CO_2 gas which was released from the reaction between HCl and Na_2CO_3 . Low conversion of CO_2 gas into

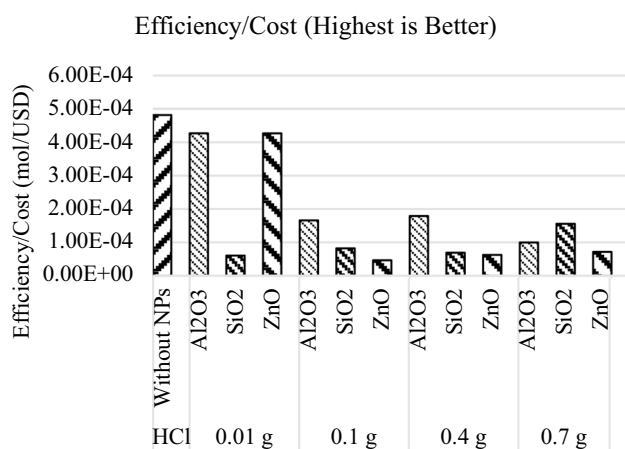


Fig. 13 Efficiency versus cost ratio of NPs in 6700 ppm Na₂CO₃

carbonic acid since HCl acid is not fully spent in the reaction. ZnO and Al₂O₃ nanoparticles show low efficiency versus cost ratio. Lower amount of bicarbonate ions remaining in the solution for these nanoparticles indicates that abundance of CO₂ gas has been released as rapid result between HCl and Na₂CO₃.

Referring to Fig. 13, Al₂O₃ and ZnO show the best efficiency versus cost. These values dropped gradually in 0.1 g of nanoparticles added into Na₂CO₃ solution. However, silica shows slightly improved efficiency compared to acidizing run in 0.01 g. The efficiency of Al₂O₃ is highest in 0.4 g of nanoparticles added in the solution, whereas silica and zinc oxide show similar efficiency. For 0.7 g of nanoparticles in 17000 ppm of Na₂CO₃, silica shows the best efficiency compared to ZnO and Al₂O₃. Overall, the performance of Al₂O₃ fluctuates for each case; meanwhile, ZnO nanoparticles demonstrate reducing efficiency. Silica, on the other hand, gives improving efficiency as the amount of nanoparticles in Na₂CO₃ solution is increased.

Conclusion

The efficiency of nanoparticles in catalyzing carbon dioxide gas into carbonic acid is further studied by using SiO₂, Al₂O₃, and ZnO in varying concentration of Na₂CO₃. Concentration of carbonic acid (H₂CO₃), bicarbonate ion (HCO₃⁻), and carbonate ion (CO₃²⁻) is analyzed based on Henry's law of solubility. Overall, silica shows the best efficiency as catalyst in 6700 ppm Na₂CO₃ solution due to high stability and dispersion in aqueous solution. Silica engages into rapid dissociation of water molecules and binds with OH⁻ group to react with CO₂ gas and form HCO₃⁻. The nanoparticles reduce the reactivity of HCl through conversion of bicarbonate ions. However, ZnO gives better efficiency in 17 000 ppm of Na₂CO₃. The efficiency of silica in

this concentration increased at 0.7 g, proving the minimum amount required as catalyst. In contrast, ZnO and Al₂O₃ have lower efficiency as acid retarder since changes in pH values affect the performance of the nanoparticles. The surface charge demonstrated by ZnO and Al₂O₃ depends on pH changes which make these nanoparticles to perform inefficiently. Overall, silica is chosen as the best catalyst due to high efficiency versus cost ratio as illustrated in Figs. 12 and 13.

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